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Contents :-

Historical	1
The thermometers	10
Apparatus	23
Results	30
Conclusion	44

54-407

On the Variation of the Specific Heat of Water.

Historical.

Regarding the earlier investigations in the Specific Heat of water very much can be said. For although many experiments in the subject have been made since it then with the exception of Regnault's seem to have been characterized by that careful determination of error, which was lacking in the determination of physical quantities.

Even Regnault did not discover the peculiar variation of

the specific heat of water which is now believed to be the true law. The experiments were conducted, principally, at high temperatures, and at temperatures above 30° or 40° C the sp heat is probably, as he found, subject to a gradual and regular increase.

Among the most important experiments — the specific heat of water — regular order the first is found to show with an error of Neumann. An account of them is given in Pogg. Ann. ~~XXIII~~. By the method of mixtures Neumann found that the ratio of

the sp. heat of water at 80°R
($= 100^{\circ}\text{C}$) is to that at ordinary
temperatures as 1.0127 is to unity.

In 1840 Regnault's experiment
has shown that at
the respective temperatures 0° ,
 10° and 80°C the sp. heat of water
is represented by the numbers
1.0000, 1.00067 1.00188.

A later value Regnault^I has
made a very accurate determina-
tion of the sp. heat of water, also
by the method of mixtures, but
extending the range of the measure-
ments to high temperatures. He found
that, calling the sp. heat between
 0° & 80°C unity, then between

30° and 110° it is 1.0005 and between 50° and 190° it is 1.015. This formula for interpolation was

$$K = 1.0005 + 0.000025T^2$$

which indicates a small but regular increase in K with the temperature.

Hansen and Nathan in 1910 measured the sp. heat of water and in it arrived at some curious results.

They are given in part in 1911 Ann. D.I. One defect of their method was the mixing, in open vessels, the water whose sp. heat they wished to determine. This proceeding not only allows evap.

The conclusion which the same
experiments [§] ~~indicated~~ ^{showed} ~~in~~ ^{was}
that water, out of a vessel ~~was~~
due to the buoyancy, and was
therefore to be rejected.

In the year 1777 I first appeared
in the ~~Journal de Physique~~ ^{Journal de Chimie} in
which paper embodying the result
of a determination of the weight
by Transbureau. In this paper the
the method of mixing was adopted,
and again the same took
place in open vessels. For these
particular experiments I
affirmed that within that the
loss was to the evaporation of
the water must have been very

would make the measurements less conducted with rapidly. Still it would appear that the error due to this cause may affect, to a considerable extent, the value of the specific heat.

~~Mathematical derivation of the~~
sp. heat K , at any temperature t is:

$$K = 1 + 0.000302t$$

showing that K increases regularly with increasing temperature.

We may be sure that this is the case 1874. Physicists generally, however, held that the specific heat of water was more constant as indicated experimentally from 0° to 100°C . During that year

however, Prof. Rowland showed by his researches on the Mechanical Equivalent of Heat, and by direct experiments, that the specific heat of water did not increase regularly with increase of temperature and that it decreased from 0° to a minimum in the neighborhood of 30° C.

Furthermore in 1882 F. Neesen of Berlin was investigating the same subject, and deducing the variation of the specific heat of water from 0° to 100° C. He found that the specific heat of water was a minimum at 30° C. and that it increased with increase of temperature. The results of his work are not inconsistent with those of Prof. Rowland.

the same as Prof. -Rauvold's they
are so qualitatively; i.e. they indicate
a decrease in the value of the sp.
heat of water from 0° to about 30° .

Coming to the second point
and importance of these conclu-
sions the experiments described in the
above paper are the result
of Prof. Rauvold's work
taken during the last few months
The experiments were made in
the laboratory of the University
and the methods of procedure
were the same as those of Prof. Rauvold
The results are as follows

The Thermometers.

For the experiments on the sp. heat
it was necessary to have two
thermometers which had been
compared either directly or indi-
rectly with the standard
so that their readings could be
finally reduced to the absolute
scale. As the University was in
possession of some standard in-
struments for which this compar-
ison had already been made
with great accuracy, it was
thought sufficient to make
the indirect comparison.

The two thermometers used in
the experiments were of the following

These were of good construction,
being furnished with a reflecting
cuvet and a small reservoir at
the top of the tube, two features
which are essential to the
scale method. They were first
calibrated, in the usual manner
which consists in measuring the
length of a short column of
mercury, which is sufficient to fill
certain portions of the thermometer
tube. During this process great
care was taken not to warm the
instrument and when it was
it was handled it was wrapped
with cloth. Taking the length

thus measured as ordinates and
 the scale readings of the middle
 of the thread as abscissae, a curve
 is drawn around the points de-
 termining the curve. The vol-
 ume of the tube is therefore
 proportional to the areas of the
 tube at the corresponding points,
 and the volume of the tube to
 any point is the sum of the
 areas to that point. The
 middle and quarter points of
 the tube, however, are measured
 as a check on the preceding work,
 and the volume of the tube
 at these points is compared with

longer than one half and one quarter the length of the tube, respectively. A tube was next constructed by measuring off ordinates on the curve corresponding to every ten degrees of the scale, which by a well known process gives the volume of the tube at any place, reckoned from an arbitrary zero, the zero of graduation being for convenience always selected. If the graduations on the thermometer scale are nearly alike the volumes at the four marked points will be very nearly alike, of course, supposing the calibration has been carefully done. In general

it is necessary to determine on the diving engine the value of the constant for each specimen and then to multiply the corresponding constant obtained by the value of the constant for the specimen to be found. If the value of the constant is not known then again it is safe to assume that the specimen is made of steel.

If it is known the value of the stem as given by the table and T the temperature on the mechanical thermometer then we have

$$T = CV - t_0$$

in which the value of the constant C must be determined.

the average velocity of diffusion
 from the temperature t to the
 temperature t' is $\frac{1}{2}(t+t')$
 and the diffusion coefficient is
 $D = D_0 e^{-\frac{U}{RT}}$ where U is the
 activation energy and R is the
 gas constant. The diffusion
 coefficient D is a function of
 temperature t and the diffusion
 coefficient D' is a function of
 temperature t' . The diffusion
 coefficient D is a function of
 temperature t and the diffusion
 coefficient D' is a function of
 temperature t' .

$$t = \frac{1}{2}(t' + t) \quad \text{and} \quad t' = t + \Delta t$$

assuming $\Delta t \ll t$ and the
 reading error is negligible
 and this becomes

$$t = C \sqrt{t' - t} \quad \text{and} \quad t' = t + \Delta t$$

In the present case, we have

same thing to occur in thermometers made of English glass.[†]

The next step, after the calibration, is the comparison. The two thermometers 108904 and 108947 were therefore placed in position as were also the two Baudin -- Baudin 6163 and 7832, and after a few minutes their zero readings taken. They were then fastened in the air thermometer case and when removed all four were found to be exactly the same. The only case was taken that the bulbs of the four thermometers should all be at exactly the same level. After adjustment, each

[†] This is an American glass thermometer, but it is not a thermocouple.

ings of the four thermometers were taken at intervals of about 3° up to 40° . In making a series of readings the thermometer was ~~not~~ turned any farther to left, then without reading the last one again from left to right. By taking the mean of these ~~the error arising from the~~ accuracy of reading all the thermometers at once is eliminated. The results of such a comparison furnish the data for the formation of the equations of condition, from which C and m are to be calculated by the method of least squares.

Station for characteristic 108954
 The following equations were
 determined:

$$0 = 109.5016 - t_0$$

$$-0.010 = 109.5016 - t_0 - 1.8 \text{ sec}$$

$$8.261 = 109.5016 - t_0 - 0.9$$

$$10.230 = 109.5016 - t_0 - 0.9$$

$$31.527 = 322.4596 - t_0 - 0.9$$

These values represent the
 measured values of the
 signal strength at various
 points yields the exact prob-
 ility of the signal.
 The other values are given in

for thermometer 108947, C and m had these values:-

$$C = .13963 \quad m = .0000140$$

and for thermometer 108954

$$C = .13917 \quad m = .0000044.$$

The comparison in all cases was made for each thermometer and the above values represent the mean of the whole number of readings in the comparison for each thermometer. The values for thermometer 108947.

$$T = .13963V - t_0 - .000014T(40 - T)\{1 - .003(T + 40)\}$$

and for thermometer 108954

$$T = .13917V - t_0 - .0000044T(40 - T)\{1 - .003(T + 40)\}$$

where T is the temperature on the air thermometer, T' the reduced

corresponding to the same reading
on the instrument depending on
the zero-point.

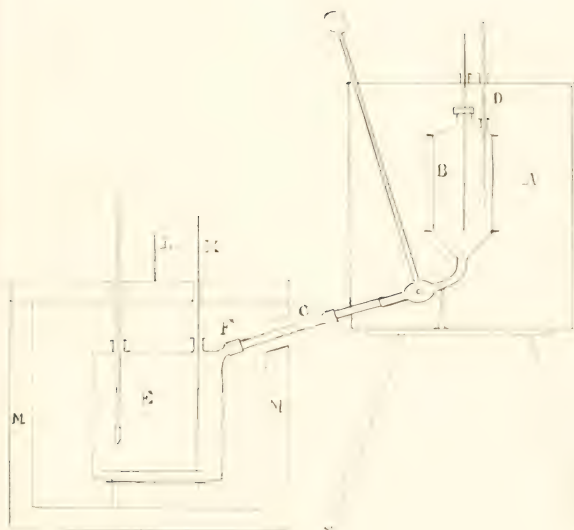
Usually, the range of temperature
is very large, and by
interpolation the intermediate ones,
the whole being combined in
a table of temperatures, which
has been copied, for each ther-
mometer, into the
Record Book. The temperatures
are then written down in the
Record Book.



-Apparatus-

The form of the apparatus used is shown in the accompanying figure.

It consisted of two reservoirs joined by a narrow tube, which was filled with water. The experiment was to be made at low or high temperature, and which was in communication, by means of a three-way stopcock, with a vacuum pump B and with the well-known apparatus C; the calorimeter E provided with



an engine - which the son
 owned of a great quantity, and
 a small yacht. He was very well
 acquainted with the submarine. The
 name of the small yacht is
 seen at 2. The name of the
 spot - which was seen when
 we were in the water - is
 in the front. As far as possible
 any change of appearance, and
 for the same purpose, the
 submarine was taken in front
 by the submarine. The submarine
 appeared to be in the
 sounding yacht.

Although when approaching
 at last the submarine the name

B was kept in place and the water from the melting ice allowed to flow through it into the lower calorimeter. As no heat was to be transferred to the water from the ice system in the vessel B, differ appreciably from zero. The opening into the stop-cock was always covered with a small piece of ice from being carried into the calorimeter with the flowing water. The calorimeter was made of very thin copper and before use was polished with emery.

After weighing the sample and
at the conclusion of the test
the sample was removed
The weight of the sample
was 388.5 gms and its calorific
capacity was 2.25 cal/gm

During the course of the experiment
the water was removed
with the aid of a vacuum
to remove the top of the
sample was removed and
solder it in place. In this
way the weight of the cal-
orific material was found
to be 2.25 cal/gm. The
resulting material was
found to be 2.25 cal/gm.

the metal being exposed to
 air, the metal being exposed to
 running water to be composed
 of, the metal being exposed to
 the air being exposed to the
 40° would be about 0.043, there-
 fore

$$0.043 \times 4 = 0.172$$

or 0.2 must be added to the
 former value of the capacity
 making it 35.6, the weight be-
 ing 392.5 grams.

The method of experiment-
 ing may be described as follows:
 The vessel A having been filled
 with broken ice, the water ther-

from the vessel A having been filled with broken ice, the water ther-

immersed them in, and, after about ten or twelve minutes, they were raised for the purpose of determining their zero position. The calorimeter in the water tank was about half filled with water, weighed, and then placed in position within the jacket; one thermometer was then introduced from the top and immersed in the water inside. After adjusting the water level some 10 degrees the temperature of the calorimeter, allowing some three or four minutes for the stop calorimeter to reach equilibrium with the water tank for radiation. Finally the stop calorimeter

was heated, water flowed from A
 and the thermometer, and the other
 thermometer being then placed
 in the water the flow of water
 was discontinued and readings
 of both thermometers taken were
 made as previously. In this
 way the final temperature of
 the mixture was determined as
 the mean of the readings of the
 two thermometers. First, without
 approaching it from above, and
 the other from below. The mean
 result thus far has been very
 nearly correct, even if thermom-
 eters, as is supposed, lag behind
 the true temperature.

Corrections for the calorific capacity of the thermometers (equal to about 1.1 gram for each) were always applied, as well as the time-correction for radiation, and that caused by the protruding stem. The temperature of the water jacket was always noted but it was found to differ so slightly from that of the air surrounding the calorimeter that it has been thought unnecessary to give it in the tables.

Experimental Results.

As an example, the following
~~experiment~~ is given in which
 together with the formula of
 reduction:-

Let W be the weight of calorimeter alone

W_1 = the weight of calorimeter +
 water before mixing water
 from vessel A.

W_2 = the weight of calorimeter +
 water after adding water
 from vessel B.

t = temperature of calorimeter
 before addition

t_1 = temperature of mixture

... (1) ...
... (2) ...
... (3) ...
... (4) ...

$$\frac{(w_1 - w)(t_1 - t) \times \text{sp. heat between } t_1 \text{ and } t_2}{(w_{II} - w)(t_{II} - t_1) \times \text{sp. heat between } t_{II} \text{ and } t_1} = \text{const.}$$

therefore,

$$\frac{\text{sp. heat between } t_{II} \text{ and } t_1}{\text{sp. heat between } t_1 \text{ and } t} = \frac{(w_1 - w)(t_1 - t_1)}{(w_{II} - w)(t_{II} - t_1)}$$

The following are the results of the experiments conducted.

W with added solder = 392.5 gms
 $w_1 = 1574.8$ $w_{II} = 2419.9$

See Appendix

Thermometer 102947. Thermometer 108954

.35 .38 .38 .00 .00 .00

108947 108,454

Time In calounich In vessel M

42 243.39 0.00

43 242.99 0.00

44 242.50 0.00

45 242.05 0.00

108,454

46 $\frac{2}{3}$ 143.50 140.60

47 $\frac{2}{3}$ 143.60 140.68

48 $\frac{2}{3}$ 143.70 140.74

These readings from time with a
 note therefore comparison of
 water in calounich with
 vessel at 108,454 in which at
 time 108,454 in 2007

Example: ...

the mean of 140.53 and 143.40.

Now,

$$241.75 \text{ cancelled } +0.19 \text{ for zero } +0.46 \text{ for stem} = 33.507$$

$$143.40 \quad " \quad +0.19 \quad " \quad -0.04 \quad " \quad " \quad = 19.741$$

$$140.53 \quad " \quad 0.00 \quad " \quad -0.04 \quad " \quad " \quad = 19.729$$

mean 19.735. Hence we have

$$W_1 - W = 1574.8 - 392.5 + 35.4 + 1.1$$

$$W_2 - W = 2419.9 - 1574.8 + 1.1$$

$$t_1 - t = 33.507 - 19.735 = 13.772$$

$$t_2 - t_1 = 19.735 - 0 = 19.735.$$

Hence

sp heat between $0^\circ - 19^\circ$

is ...

$$\frac{(241.99 - 1574.8 + 1.1) 19.735}{(241.99 - 1574.8 + 1.1) 19.735}$$

$$(241.99 - 1574.8 + 1.1) 19.735$$

$$= 1.0034$$

3

Table I (continued)

Table II

Vertical angles of the 3rd kind

-bottom-

-crossed- angles

$$\frac{2^{\circ}-13^{\circ}}{20-37} = 1.00074$$

$$\frac{3^{\circ}-12^{\circ}}{20-37} = 1.00064$$

$$\frac{3^{\circ}-17^{\circ}}{17-37} = 1.0015$$

$$\frac{4^{\circ}-23^{\circ}}{21-28} = 1.0030$$

$$\frac{23^{\circ}-27^{\circ}}{27-31} = 0.9975$$

$$\frac{37^{\circ}-24^{\circ}}{24-31} = 0.9957$$

$$\frac{4^{\circ}-17^{\circ}}{17-25} = 1.0020$$

$$\frac{4^{\circ}-23^{\circ}}{21-27} = 1.0034$$

$$\frac{20^{\circ}-24^{\circ}}{24-27} = 0.9956$$

Table II (continued)

Radical values of $\sqrt{13n-2}$	
Index	Radical value
$\frac{21-29}{29-36} = 0.9980$	$\frac{21-29}{29-36} = 0.9980$
$\frac{0-20}{20-33} = 1.0003$	$\frac{0-20}{20-33} = 1.0003$
$\frac{0-24}{24-30} = 1.0000$	
$\frac{0-21}{21-31} = 1.0044$	$\frac{0-18}{18-30} = 1.0067$
$\frac{0-19}{19-24} = 1.0007$	
$\frac{0-23}{23-36} = 1.0028$	$\frac{0-21}{21-34} = 1.0062$

The following observations are on the absolute scale. The water in the vessel is at a constant temperature in the thermodynamic state. In the bottle the liquid is allowed to come to the height of the thermometer and the water is then added from vessel A. The next eight indicate the readings of the thermometer, temperature of surrounding air, correction for protruding stem, and finally the temperature of the water. The ratios of the sp. heat of the water to the sp. heat of the liquid will be found in the

next table where they are also
compared with the figures al-
ready given by Prof. Rauland.
Although it was attempted to
make the same comparison with
the data in many cases this
was impracticable, and in
some cases the data have been
occasionally left. Where the
temperature intervals are comp-
arable, however, it will be
marked that there is good
agreement with the results.

It may be interesting to
further compare these values
with those which can be
deduced from the tables given

in Prof. Rowlands' paper on the mechanical equivalent of Heat. This is very easy to do, from the fact that the mechanical equivalent can be directly as the specific heat. It is therefore only necessary to plot a curve with the values of the mechanical equivalent at different temperatures as ordinates and temperatures as abscissae. If one then takes off ordinates which can be taken as averages between the required limits of temperature, and divide one set by the other, one may obtain results which

expresses the ratios of the specific heat between the same degrees of temperature.

A glance at the following table will show how these compare with the results of other and direct determinations. It will be remarked that, while in no case — with the exception of Neesen's — do the figures differ greatly, among themselves, with others, to a slight discrepancy in the estimation of the function of the expansion. The values obtained from the expansion of the coefficient of heat capacity

Temperature and Time

Interval	Value	Wavelength	Frequency	Wavelength
<u>0-14</u> 14-17	1.00000			0.0030
<u>0-17</u> 17-22	1.00000	1.00027		1.00015
<u>0-17</u> 17-29	1.00067	1.00020	1.00070	
<u>0-18</u> 8-27	1.00053	1.00025	1.00020	
<u>0-19</u> 19-30	1.00000	1.00000	1.00111	1.00057
<u>0-19</u> 19-33	1.00066	1.00000		1.00000
<u>0-20</u> 20-31	1.00000			1.00000
<u>0-21</u> 21-35	1.00060	1.00045	1.00058	1.00000

Temperature	Med. Temp.			
Date	Value	Rowland	Neesen	Value
$\frac{0-13}{13-13}$	1.0000	—	—	1.0000
$\frac{1-23}{23-13}$	0.0435	—	—	0.0435
$\frac{11-23}{23-13}$	0.5385	—	—	0.5385
$\frac{20-23}{23-13}$	0.8462	—	—	0.8462
$\frac{20-23}{23-23}$	1.0000	.9933	.9970	.9981
$\frac{21-23}{23-23}$	1.0000	—	—	1.0000
$\frac{22-23}{23-23}$	1.0000	.9933	—	.9981
$\frac{23-23}{23-23}$	1.0000	—	—	1.0000
$\frac{24-23}{23-23}$	1.0000	—	—	1.0000
$\frac{25-23}{23-23}$	1.0000	—	—	1.0000
$\frac{26-23}{23-23}$	1.0000	—	—	1.0000

possible, however, to determine the maximum temperature.

There seems to be no serious doubt as to the validity of the results obtained in the methods of experiment which have been applied to the present discrepancy, and indeed at present there can be no importance attached to a knowledge of the exact position of the maximum.

It is sufficient to know that the specific heat of water does decrease from zero to a point between twenty and thirty degrees centigrade - a conclusion which is being widely accepted from all the facts before us.

G. A. Briggs

